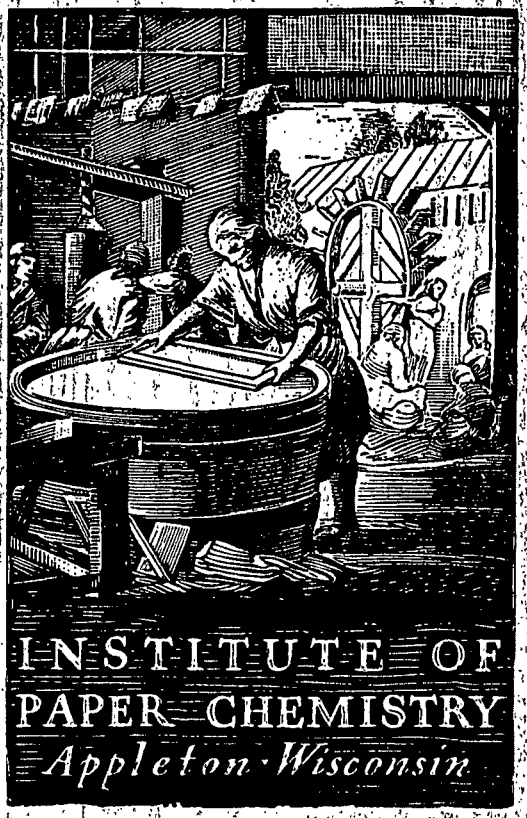

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

Project 3143

Report Three

A Progress Report

to

MEMBERS OF GROUP PROJECT 3143

September 16, 1974

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

SUMMARY

This report covers studies of the flocculation of TiO_2 by various polymer systems and of the retention of TiO_2 in sheets formed in a standard sheet mold and in the IPC pressure sheet mold.

The effect of molecular weight on the efficiency of the flocculation aid was examined. No dependence on molecular weight of either maximum flocculation attained or amount of polymer required to achieve optimum flocculation was found for a series of cationic polyacrylamides. Companion studies of adsorption of these polymers onto the TiO_2 surface indicate only a tiny fraction ($\sim$ 1%) of the surface is covered with polymer under the best flocculation conditions. Less than one macromolecule per two particles produces maximum effect for these high molecular weight ($\sim$ 1 million) materials. These results collaborate those described in Progress Report Two for a series of sodium polystyrene sulfonates (NaPSS) with either alum or polyethylenimine (PEI) as a positively charged intermediary. A study of the amount of PEI necessary for optimum flocculation as a function of TiO_2 concentration revealed a direct proportionality between the two. An investigation into whether flocculated and unflocculated TiO_2 at a given dosage of polymer have the same or different zeta potentials yielded ambiguous results.

A series of cationic (modified polyacrylamides) and of anionic (NaPSS plus PEI) retention aids were studied using standard handsheet formation. No trends with molecular weight of either maximum retention of TiO_2 achieved or of the amount of polymer necessary for best retention were observed for either of the

two systems. Doubling the amount of TiO_2 in the furnish required no additional polymer for maximum retention indicating that the major portion of the retention aid is adsorbed by the pulp. The pH at which the cationic retention aid was added to the TiO_2 was found to have a strong effect on the latter's optical efficiency. Mixing of the two components (whether in the presence of the pulp or not) at low pH where many of the amine groups are protonated induced irreversible flocculation of the TiO_2 particles. These agglomerates when subsequently adsorbed by the pulp yielded a decreased specific scattering coefficient at a given level of retention. Mixing the two components at high pH where the amine groups are largely unprotonated prevented the flocculation. The origin of the large, negative zeta potential at optimum retention conditions could not be explained by either counterion binding to the polymer or adsorption of submicroscopic fines onto the initially positively charged TiO_2 particles.

The IPC dynamic drainage tester was modified to permit sheet formation and removal for optical and retention analysis. Sheets were formed at three different drainage rates and with various retention aids. Differences in retention level but not in resistance to hydrodynamic shearing were found by varying the molecular weight of the polymer. The expected trend of a decrease in retention with increase in drainage rate was found in all cases.

INTRODUCTION

This report covers the work of the last six months and is divided for convenience of presentation into three parts.

The first part deals with essentially flocculation considerations. The role of molecular weight of the flocculant is examined by utilizing a series of cationic polyacrylamides. Studies of the adsorption of the polymers onto TiO_2 yielded information useful in interpreting the flocculation behavior of the system. The balance of the section describes experiments which probe the details of the flocculation process.

The second part concerns retention experiments using standard handsheet formation. The effects of molecular weight of both anionic and cationic retention aids are examined. A number of experiments were carried out to try to obtain a better understanding of the large negative zeta potential found previously (1) under conditions of maximum retention.

Agitation of the pulp/pigment system occurs at a number of points in the papermaking system subsequent to the addition of the retention aid. Different types and degrees of agitation occur at pumps, in the headbox, through the slice and during drainage on the wire. The third part of this report is concerned only with the latter aspect. The retention of TiO_2 in the sheet was studied by using the modified dynamic drainage tester. The major thrust here was to study the effect of drainage rate on retention and to determine whether the molecular weight of the retention aid played a part in the resistance against loss of pigment during sheet formation on the wire. Information concerning the drainage properties of the furnish was simultaneously generated and is interpreted.

PART I. ADSORPTION AND FLOCCULATION-TiO_2 PLUS POLYMERS

MATERIALS AND METHODS

In the series of experiments to be described here the TiO_2 and PEI (polyethylenimine) were the same as used previously (1). In addition three samples of modified polyacrylamides were generously supplied by The Dow Chemical Company. These cationic polyelectrolytes were specially prepared to all have the same chemical structure, and hence the same degree of protonation at a given pH, and to differ only in molecular weight. According to the manufacturer (2) these latter were approximately 0.5×10^6, 1×10^6 and $>> 1 \times 10^6$. They will be designated as Dow L, Dow M, and Dow H, respectively, and have been used in other studies at the Institute (3). These polymers have a high charge density with theoretically 80% of the monomer units having been modified to incorporate tertiary amine groups (2).

The flocculation experiments were carried out as described previously (1). Adsorption isotherms for the three Dow polymers on TiO_2 at pH 5 were determined. The procedure was that used previously (1) except for the method of determination of the amount of polymer remaining unadsorbed. Here a Beckman Process Carbonaceous Analyzer with a range of 1-100 ppm total carbon was employed. The instrument was calibrated with samples containing either known amounts of the polymers or blanks comprising the make-up water.

RESULTS AND DISCUSSION

Adsorption of Dow Series on TiO_2

The experiments consisted of mixing various concentrations from 10 to 100 mg/liter of the Dow polymers with 7400 mg/liter of TiO_2 for 5 minutes. The

amount remaining unadsorbed was then determined and the amount adsorbed by difference. As previously found for the PEI/TiO_2 system (1), the adsorption isotherm for the present results was of the Langmuir type. A plateau region was reached for polymer concentrations greater than 50 mg/liter corresponding to maximum surface coverage. The data were analyzed in terms of the Langmuir Equation (4). The characteristic plots were linear and the derived parameters, C_M^*, the maximum amount of polymer the surface will absorb, and K, the "affinity" constant, are listed in Table I.

TABLE I

LANGMUIR PARAMETERS FOR THE ADSORPTION OF THE DOW POLYMERS ON TiO_2 AT A CONCENTRATION OF 7.4 G/LITER AND A pH OF 5.0

Polymer	C_M^*, mg/liter	K, liter/mg
Dow L	32.0	0.16
Dow M	25.5	0.13
Dow H	25.5	0.10

The amount adsorbed at saturation, C_M^*, is similar to that found previously for PEI (1), but the "affinity" constants, K, are about an order of magnitude smaller suggesting a weaker interaction between the present polymers and the TiO_2 surface.

Flocculation by PEI: Effect of Concentration of TiO_2

In the previous report (1) the flocculation of TiO_2 at a concentration of 1000 mg/liter by PEI was studied. Because particle concentrations much lower than this would be expected in the white water and in the mill sewer water, it was of interest to determine whether PEI could be used to flocculate

TiO_2 at these lower concentrations. If so, is there a relationship between the relative amounts of TiO_2 and of PEI for maximum flocculation?

Accordingly, TiO_2 at a pH of 5 and at concentrations of 500, 250, 125, 50, and 25 mg/liter was treated with various concentrations of PEI, and the degree of flocculation was observed by the optical transmittance technique (1). The results are shown in Fig. 1 where the transmittance is plotted against the logarithm of the PEI concentration at the indicated TiO_2 concentrations. (It will be recalled that a T of 160 μa is obtained for pure water.) As the amount of TiO_2 is reduced, there is a monotonic decrease in the amount of PEI required for optimum flocculation. In Fig. 2 a doubly logarithmic plot of the concentration of PEI at the maximum flocculation conditions against the concentration of TiO_2 is presented. A straight line with unit slope provides a reasonable fit to the data. The equation for the line drawn is:

$$C_i = 3.2 \times 10^{-4} C_p \qquad (1)$$

where C_i is the concentration of PEI added and C_p is the concentration of TiO_2. For comparison the Langmuir adsorption isotherm predicts [Equation (9) of the previous report (1)].

$$C_i = [\theta/K (1 - \theta)] + C_M^* \theta \qquad (2)$$

where θ is the ratio of the amount of polymer adsorbed to the maximum amount that can be adsorbed, C_M^*. If it is assumed that there is a simple proportionality between C_M^* and the amount of surface, C_p, that is

$$C_M^* = k C_p \qquad (3)$$

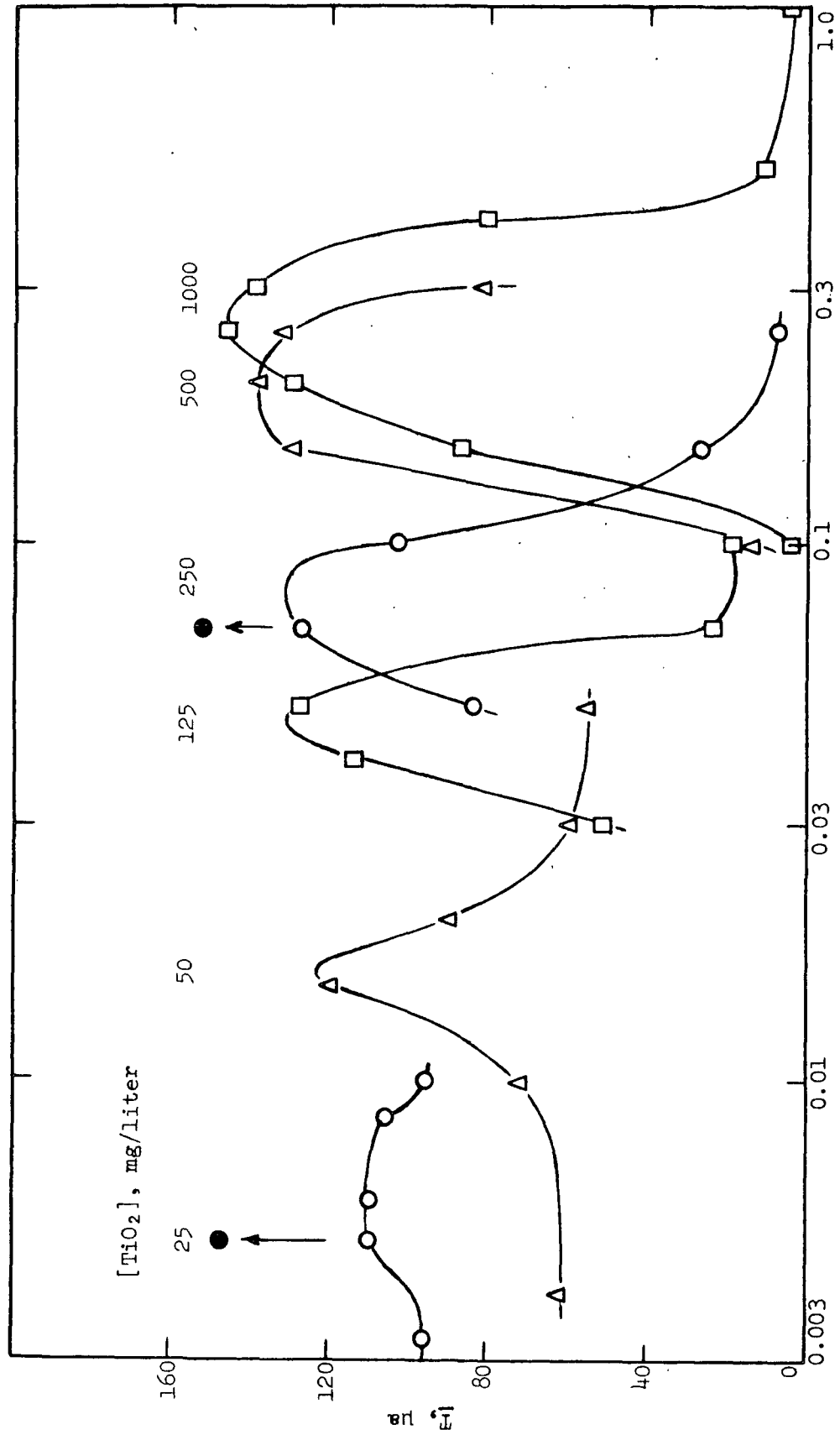

Figure 1. Flocculation as a Function of Concentration of TiO_2. Semilogarithmic Plot of Transmittance Against Concentration of PEI at the Indicated TiO_2 Concentrations

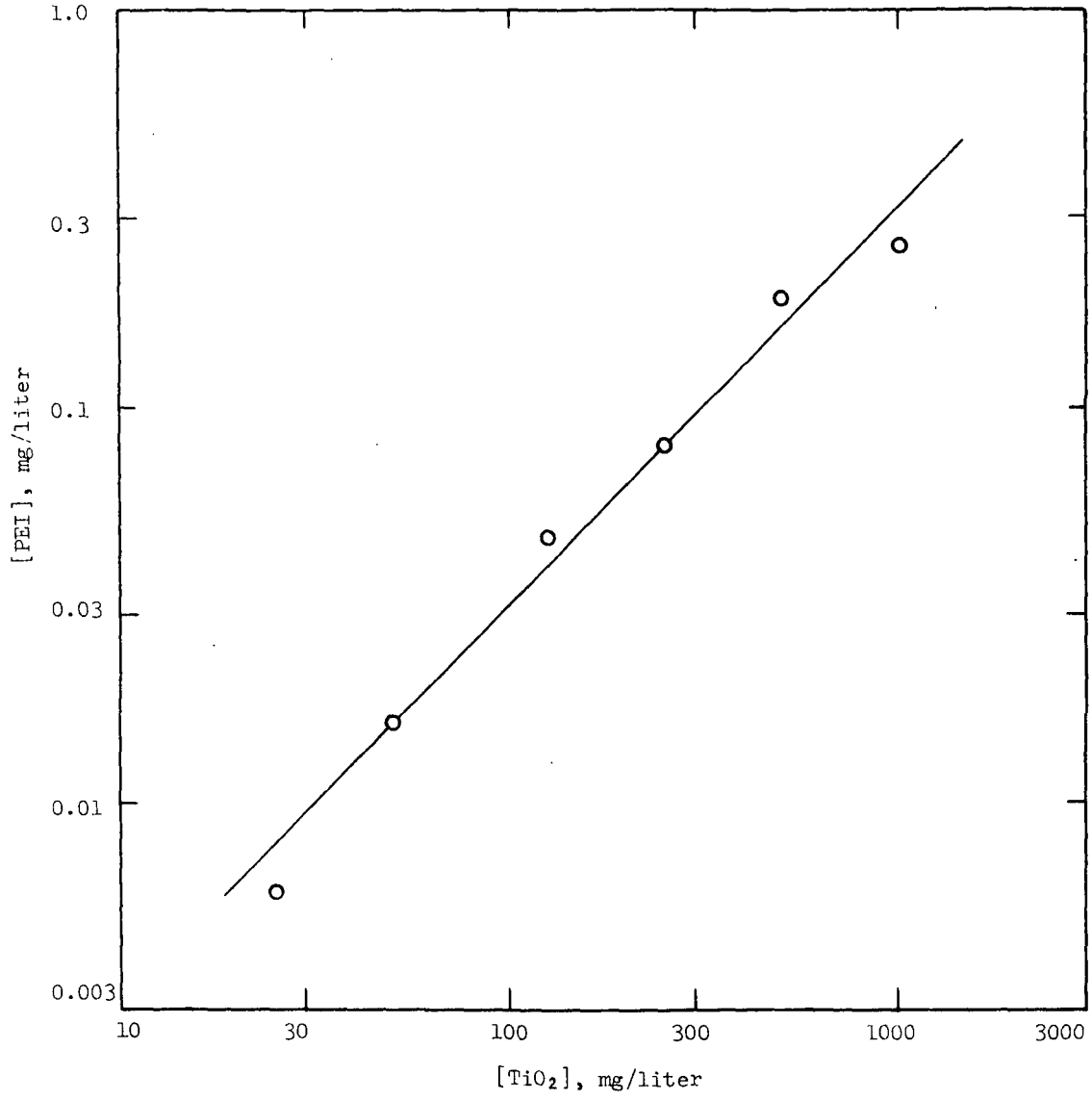

Figure 2. Doubly Logarithmic Plot of Optimum PEI Concentration for Maximum Flocculation Against TiO_2 Concentration. Line was Drawn with Slope of 1

Equation (2) can be rewritten as:

$$C_i = [\theta/K\ (1 - \theta)] + k\ \theta\ C_p. \qquad (4)$$

This equation can now be compared with Equation (1). If it is assumed that optimum flocculation regardless of particle concentration occurs at a constant fractional surface coverage, θ, the two equations are inconsistent. There are (at least) two ways out of this dilemma. (1) Although it seems intuitively reasonable, it may not be that θ is constant. Taking this latter path one can equate the right-hand sides of Equations (1) and (4) and solve for θ in terms of the various constants and C_p. The result is that at high particle concentrations θ becomes independent of C_p and approaches a limiting value of about 0.16. At lower TiO_2 concentrations this fraction is less and in the limit of low concentrations becomes directly proportional to C_p. For the two extremes of particle concentration studied here, 1000 and 25 mg/liter, the θ calculated in this way are 0.13 and 0.012, respectively. (2) The assumption that the data fit the Langmuir isotherm at all concentrations may be in error. The isotherm was obtained at a high concentration (7400 mg/liter TiO_2) and subsequent calculations at the lower concentrations were based on the extrapolation of these data. The adsorption data itself were (of necessity) taken in the restabilization region of the flocculation curve; hence extrapolation into the region of maximum flocculation (i.e., lower polymer concentrations) may be moot. Of the two explanations offered the latter would appear to be the more likely.

Flocculation by PEI: Effect of Agitation

In addition to the decrease in polymer concentration necessary to flocculate the decreasing amounts of TiO_2 seen in Fig. 1, another trend is evident. The efficiency of the flocculation process appears to decrease with

decreasing TiO_2 concentration. At the optimum, for 1000 mg/liter TiO_2, less than 5 mg/liter remain in suspension, while for the case with an initial TiO_2 concentration of 25 mg/liter, about 18 mg/liter remain. Further experiments showed that the effect was merely one of collision frequency, i.e., the standard method of mixing, employing a magnetic stirring bar at moderate speed for 5 minutes, produced too few particle collisions at the lower TiO_2 concentrations for effective flocculation. It was found that the situation could be remedied by either extending the mixing at the same speed or by increasing the mixing speed for the 5-minute time period. The effect of either of these treatments is to increase the total number of particle-particle collisions. As an example, the black symbols in Fig. 1 show the extent of flocculation caused by employing the normal mixing rate for 30 rather than 5 minutes. In both cases, 25 and 250 mg/liter TiO_2, less than 5 mg/liter remain. As mentioned above, mixing for 5 minutes at high speed produced the same result. In additional experiments not reported here it was found that for low TiO_2 concentrations, increasing the mixing rate (for a constant period of time) shifted the whole transmittance — polymer concentration curve upward but that the optimum polymer concentration for maximum flocculation remained unchanged. The lesson to be learned here is that ample time must be allowed for sufficient collisions to produce effective flocculation when working with dilute suspensions. The theory for this was, of course, long ago worked out by Smoluchowski (5) for the cases of collision by Brownian motion alone and for collisions induced additionally by laminar velocity gradients. For the present experiments, however, the shearing conditions are too ill-defined to permit application of the theory.

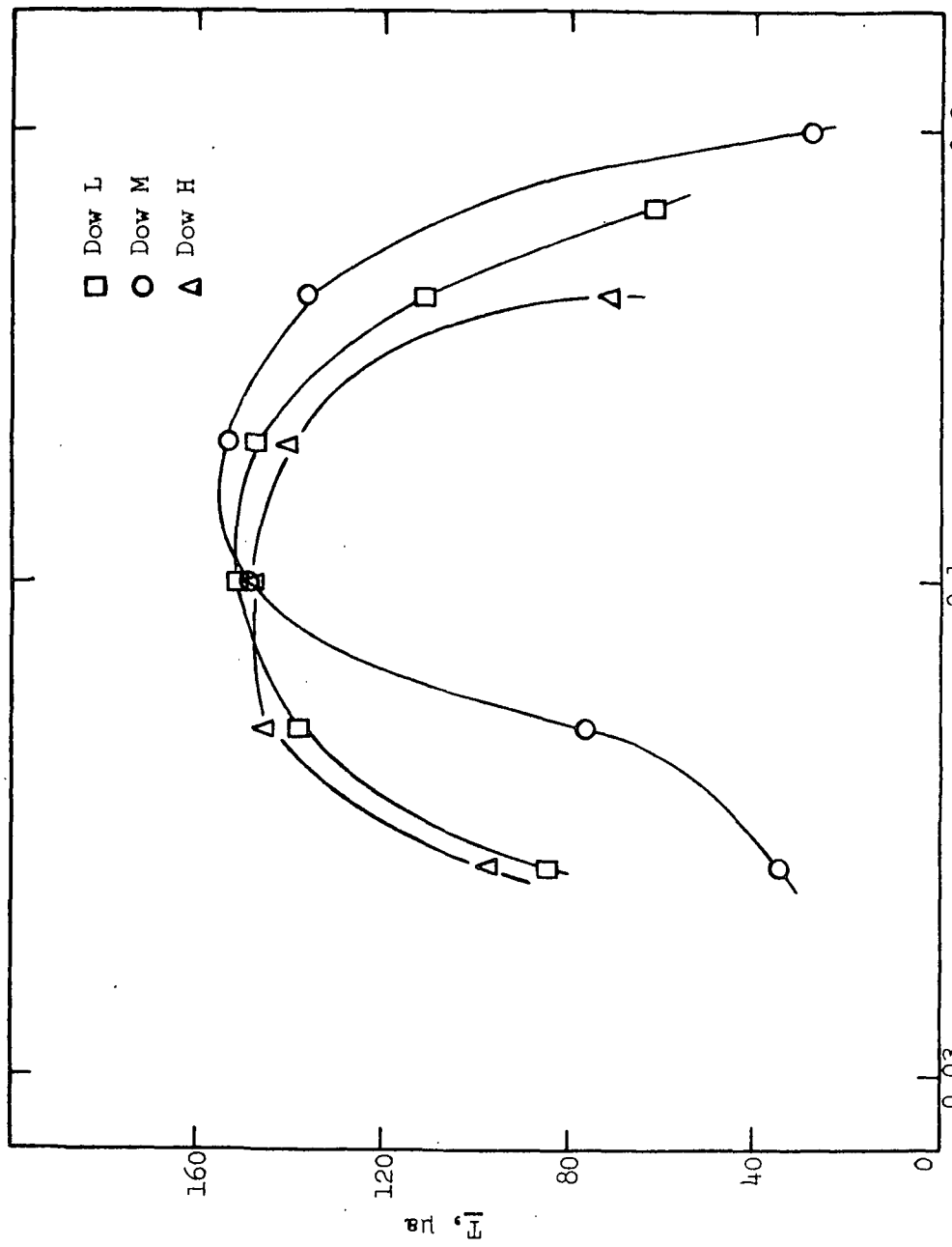

Figure 3. Flocculation of 250 mg/liter TiO_2 by Cationic Polyacrylamides. Semilogarithmic Plot of Transmittance Against Polymer Concentration for the Three Polyelectrolytes

Flocculation by Cationic Polyacrylamides — Effect of Molecular Weight

The results for flocculation of TiO_2 (250 mg/liter) by various concentrations of the Dow series at a pH of 5 are shown in Fig. 3. As found previously for flocculation of PEI-treated TiO_2 by sodium polystyrene sulfonate (1) there is little effect of molecular weight on the optimum concentration of polymer for most effective flocculation.

Two other recent reports reached the same conclusion. Gregory (6), studying the flocculation of polystyrene latices by quaternized polyamines, and Lindquist (7), studying the flocculation of Ludox silica by PEI in the protonated state, found no influence of molecular weight on the flocculation process. In contrast, the latter author (7) found a strong dependence on molecular weight when the PEI was uncharged (pH = 11). He explained these results by postulating that in the case of uncharged (or weakly charged) polymers, the flocculation occurs by La Mer type bridging, the longer molecules being more effective in bridging the gap between particles. For the case of highly charged polymers he argues for the "patch" theory (6, 8). Here the cationic macromolecule adsorbs onto the negative surface to produce a local area of high positive charge density. This area then interacts strongly by electrostatic attraction with a negative area (containing no adsorbed polymer) on an adjacent particle. In this picture (8), to a good approximation, the important parameter is the total weight of polymer adsorbed (or total charge) with the molecular weight playing only a weak secondary role. The results of the present study also appear to fit this view.

The concentration of the Dow polymers necessary for maximum flocculation (0.10-0.13 mg/liter) may be compared with that of PEI (0.08 mg/liter) from Fig. 1 at the same TiO_2 concentration. Although the two types of polymers

have widely differing chemical structures and molecular weights, the concentrations required are very nearly the same. Polyethylenimine apparently is slightly more efficient than the modified polyacrylamides, and a similar trend will be seen in the retention results to be discussed subsequently.

It is of interest to calculate the fraction of surface covered, $\theta_{\underline{m}}$, under the conditions of optimum flocculation. If one accepts the validity of the Langmuir adsorption isotherm for these low θ (see earlier discussion), the fractional coverage can be calculated from the constants in Table I and the equations in Appendix I of Progress Report Two (1). The derived values for Dow L and Dow M are presented in Table II along with the corresponding parameters for PEI for comparison.

TABLE II

ADSORPTION PARAMETERS FOR VARIOUS POLYMERS ON TiO_2

(Concentration of TiO_2 is 250 mg/liter or 3.54×10^{13} particles/liter)

Polymer	$\underline{M} \times 10^{-3}$	$C^*_{\underline{M}}$, mg/liter	$\eta_{\underline{s}}$ [a]	$\theta_{\underline{M}}$	$\eta_{\underline{m}}$ [b]
Dow L	500	1.08	37	0.013	0.48
Dow M	1000	0.86	15	0.014	0.21
PEI	6	0.53	1450	0.066	96

[a] $\eta_{\underline{s}}$, number of polymer molecules/TiO_2 particles at surface saturation.
[b] $\eta_{\underline{m}}$, number of polymer molecules/TiO_2 particle at maximum flocculation.

Although the total weight of polymer adsorbed at saturation is within a factor of two for the three polymers, the other parameters in Table II vary considerably because of the wide differences in molecular weight. It is perhaps surprising that the optimum conditions for flocculation for the Dow polymers

occur at only a little over 1% of the TiO_2 surface covered with polymer and that for Dow M this works out to approximately one polymer molecule being shared by five particles. When the relative sizes of the macromolecules and the particles are considered, these results appear more reasonable. The roughly spherical, highly branched PEI molecule has a solution diameter (7) of about 70 A which is only about 5% of the diameter of the TiO_2 particles ($\underline{D}$ = 1520 A) and occupies an insignificant area on the latter's surface. In contrast, the modified polyacrylamides are linear molecules which exist as rather extended chains due to the intramolecular repulsion of the cationic charges (9). Although the chain is not a stiff rod, the contour length calculated assuming that it is, provides a useful measure of the domain of the polyelectrolyte. For Dow M the contour length is approximately 2 μm to be compared with the TiO_2 particle circumference of about 0.5 μm. It is readily apparent that a single macromolecule can be distributed over a considerable portion of the particle and thereby act as points of attachment for several other particles. Alternatively, the particles might be viewed as attached to the macromolecule (at least in the early stages of the aggregation process) much as charms are attached at intervals on a charm bracelet. These might later consolidate to form a rigid mass. In any case, as pointed out earlier, it is not the molecular weight, but only the total mass of polymer (or total number of charges) that determines whether flocculation will occur.

It should be emphasized that the action of the polyelectrolyte is not to merely neutralize the negative charges on the TiO_2, as when coagulation is effected by simple electrolytes containing ions that can be specifically adsorbed such as aluminum or ferric ion. Under the conditions of maximum flocculation the particles retain a net strongly negative charge.

The Zeta Potential of Partially Flocculated TiO_2

In experiments previously reported (1), the zeta potential used to characterize a flocculated system was that measured on the supernatant suspension that did not settle (or centrifuge) readily. The question might be asked: are these particles truly representative of the flocculated system? Another way of putting the same question is: if some of the particles flocced under a given set of conditions, why did not all the particles floc? A series of experiments were performed to try to answer these questions.

A suspension of TiO_2 (250 mg/liter) at a pH of 5 was mixed at moderate speed for either 5 or 30 minutes with 0.07 mg/liter of PEI, which concentration is near the optimum (see Fig. 1). The suspension was then gently centrifuged to bring down all flocculated material and the supernatant was examined with the Zeta-Meter. The sediment was slurried up with distilled water preadjusted to a pH of 5 and the particle electrophoretic mobilities were likewise measured. The results are presented in Table III.

TABLE III

ZETA POTENTIAL OF FLOCCULATED AND UNFLOCCULATED TiO_2

	ζ, mv
5 Minute mixing	
Supernatant	-16
Sediment	-5 to -12
30 Minute mixing	
Supernatant	-16
Sediment	0 to -10

It is seen that there is a range of values for the sedimented material and that in general these values tend to be smaller in magnitude than those for the unflocculated (supernatant) particles. In another experiment the same concentrations of polymer and TiO_2 were mixed for 5 minutes, the suspension without centrifuging was diluted with water preadjusted to a pH of 5, and the zeta potential was quickly measured. Again a range of values from -10 to -16 mv was obtained; these particles should include both flocculated and unflocculated TiO_2. Finally a similar experiment to the first mentioned was carried out with only the concentration of polymer being changed. The PEI concentration was 0.14 mg/liter representing an overdosed or partially restabilized system. Here the sediment and supernatant particles both had the same zeta potential, -13 mv, and the sediment did not display the range of mobilities seen previously. A facile interpretation of these experiments is not evident. The results in Table III suggest that the sedimented (or flocculated) material contains a higher (and more variable) dosage of PEI than does the unflocculated TiO_2. This would indicate that the initial mixing of polymer and TiO_2 is imperfect so that an uneven distribution of the macromolecules among the TiO_2 particles occurs. The question remains whether the zeta potential of the supernatant particles are truly indicative of the electrical state of the system. Based on its usefulness in correlating results as seen in Progress Report Two (1), the answer must be in the affirmative. Although the absolute magnitudes of the flocculated and unflocculated materials may be different (and the above results do not constitute a conclusive test of this), the trends of the two are certainly parallel and permit useful interpretations.

CONCLUSIONS

Based on the results of this and the previous report, it is apparent that in the flocculation of charged particles by oppositely-charged polyelectrolytes, the molecular weight of the macromolecule plays only a minor if not insignificant role. Furthermore, it is not necessary to completely neutralize the particle's charge by polymer adsorption; optimum flocculation conditions can occur with the particles still bearing a strong net charge. It would appear that polyelectrolytes having a high charge density (number of charges per unit length of chain or per unit weight of chain) would be more efficient flocculants than those with a lower charge density.

PART II. RETENTION OF TiO_2 ON HANDSHEETS

MATERIALS AND METHODS

The TiO_2 and polymers were the same as described previously (1), and also earlier in the present report, except that an additional cationic polymer was examined. The latter, Bubond 64, was kindly furnished by the Buckman Laboratories, Inc. It was reported by the manufacturer (10) to be a graft copolymer containing quaternary ammonium groups and a molecular weight of about one million.

For most of the experiments the pulp was the same as that employed previously (1). However, for one set of experiments the pulp was classified to remove the major portion of the fines. Classification was carried out on the Bauer-McNett classifier according to standard procedures. The disintegrated pulp was collected on stainless steel screens of 14, 20, 35, and 100 mesh and washed for 20 minutes with deionized water. The pulp from the four screens was then combined, thoroughly mixed, and used for handsheet formation.

To simulate a pulp with no fines, cut rayon fiber 0.1-inch long and 1.5 denier was used. These were specially prepared by FMC Corporation and had no surface treatment. Except for the low conformability due to their being a solid rod and the lack of fibrillation, as observed by the scanning electron microscope, these fibers should mimic ordinary wood pulp reasonably well.

RESULTS AND DISCUSSION

The data for the handsheets for set numbers greater than 50 are presented in Table IV. The data for the earlier sets were reported previously (1) and will not be repeated here although reference will be made to them. Table IV lists

TABLE IV

HANDSHEET PROPERTIES

Set No.	Additive		ζ, mv	R, %	S, cm^2/g	Tensile Strength, kg/cm
	Type	Amount, mg/40 g pulp				
51	Tydex V-70	310 100	-8	48	473	2.41
52	Tydex V-70	310 150	-24	70	513	2.51
53	Tydex V-70	310 200	-17	70	522	2.71
54	Tydex V-70	310 300	-37	66	508	2.75
55	Reten 300[a]	97	-16	74	538	1.97
56	Tydex V-700	310 100	-20	40	450	2.65
57	Tydex V-700	310 150	-20	60	486	2.51
58	Tydex V-700	310 200	-22	76	510	2.62
60	Reten 300[a]	72	-21	70	539	1.97
61	Chitosan	26	-22	77	584	1.82
63	Tydex V-700	310 300	-20	73	494	2.51
64	Tydex V-700	310 400	-16	62	474	2.89
66	Tydex	100	-15	74	555	2.29
70	PEI	50	-17	77	583	1.92
71	Chitosan	39	-27	49	493	2.10
75	Tydex	27	-26	77	582	1.82
76	PEI[b]	50	-22	78	542	1.50
77	Tydex NaCl (0.001M)	50	-19	81	578	2.00
78	Tydex NaCl (0.005M)	50	-23	73	562	2.01
80	Tydex Na_2SO_4 (0.001M)	50	-27	73	562	2.00
81	Tydex Na_2SO_4 (0.00167M)	50	-23	67	541	2.06

TABLE IV (Continued)

HANDSHEET PROPERTIES

Set No.	Additive: Type	Additive: Amount, mg/40 g pulp	ζ, mv	R, %	S, cm^2/g	Tensile Strength, kg/cm
82	Tydex Na_2SO_4 (0.005M)	50	-21	55	500	2.03
83	Chitosan	52	-18	35	457	2.23
91	Chitosan	19.5	-20	72	585	1.77
108	Tydex[c]	50	-24	60	511	
110	Dow H	50	-20	85	569	
111	Dow M	50	-15	82	566	
112	Dow L	50	-16	82	560	
113	Bubond 64	50	-19	67	549	
115	Dow H	33	-18	81	552	
116	Dow M	33	-19	72	538	
117	Dow L	33	-18	81	556	
118	Bubond 64	33	-23	71	551	
119	Dow H	6.7	-22	53	382	
120	Dow M	6.7	-22	34	426	
121	Dow L	6.7	-24	34	436	
122	Bubond 64	6.7	-27	44	480	
123	Tydex[d]	50	-15	82	742	
124	Tydex[d]	100	-26	79	705	
126	Tydex[d]	27	-23	63	678	
128	Tydex[d]	200	-11	33	512	
129	Dow H	100	-15	70	537	
130	Dow M	100	-11	79	547	
131	Dow L	100	-12	68	547	
132	Dow H	73	-13	82	583	
133	Dow M	73	-16	89	591	
134	Dow L	73	-24	88	593	
135	Bubond 64	20	-23	62	557	
136	Bubond 64	13.3	-25	59	537	
137	Tydex[e]	50	-27	4	230	

TABLE IV (Continued)

HANDSHEET PROPERTIES

Set No.	Additive: Type	Additive: Amount, mg/40 g pulp	ζ, mv	R, %	s, cm^2/g	Tensile Strength, kg/cm
138	Dow M	50	-10	83	575	
139	Dow M[a]	50	-16	80	536	
140	Dow M	20	-20	64	528	
141	Dow M[a]	20	-29	64	516	

[a]Polymer add to pulp after TiO_2.
[b]Classified pulp.
[c]HCl used for pH adjustment.
[d]10% TiO_2 on pulp.
[e]Rayon fibers.

the kinds and amounts of additives, the percentage retention, R, of TiO_2, zeta potential of the white water, specific scattering coefficient, s, and the tensile strength of the sheet.

The Effect of Molecular Weight-Anionic Retention Aid (Sets 23-30, 40, 41, 50-54, 56-58, 63, 64)

To permit effective retention of TiO_2 on pulp, both containing a negative charge, by an anionic polymer, it was first necessary to treat the pulp and TiO_2 surfaces to render them positively charged. This was accomplished by mixing them with Tydex 12 (polyethylenimine) prior to the addition of the negative polymer. Sufficient Tydex 12 was added (310 mg/40 g pulp) so that the surfaces were made strongly positive and no retention could be attributed to the Tydex 12 (cf. Set 21). Various amounts of the V-series of sodium polystyrene sulfonates were then added to the several sets as the retention aid. The results are shown in Fig. 4 where V-70, V-500, and V-700 have average molecular

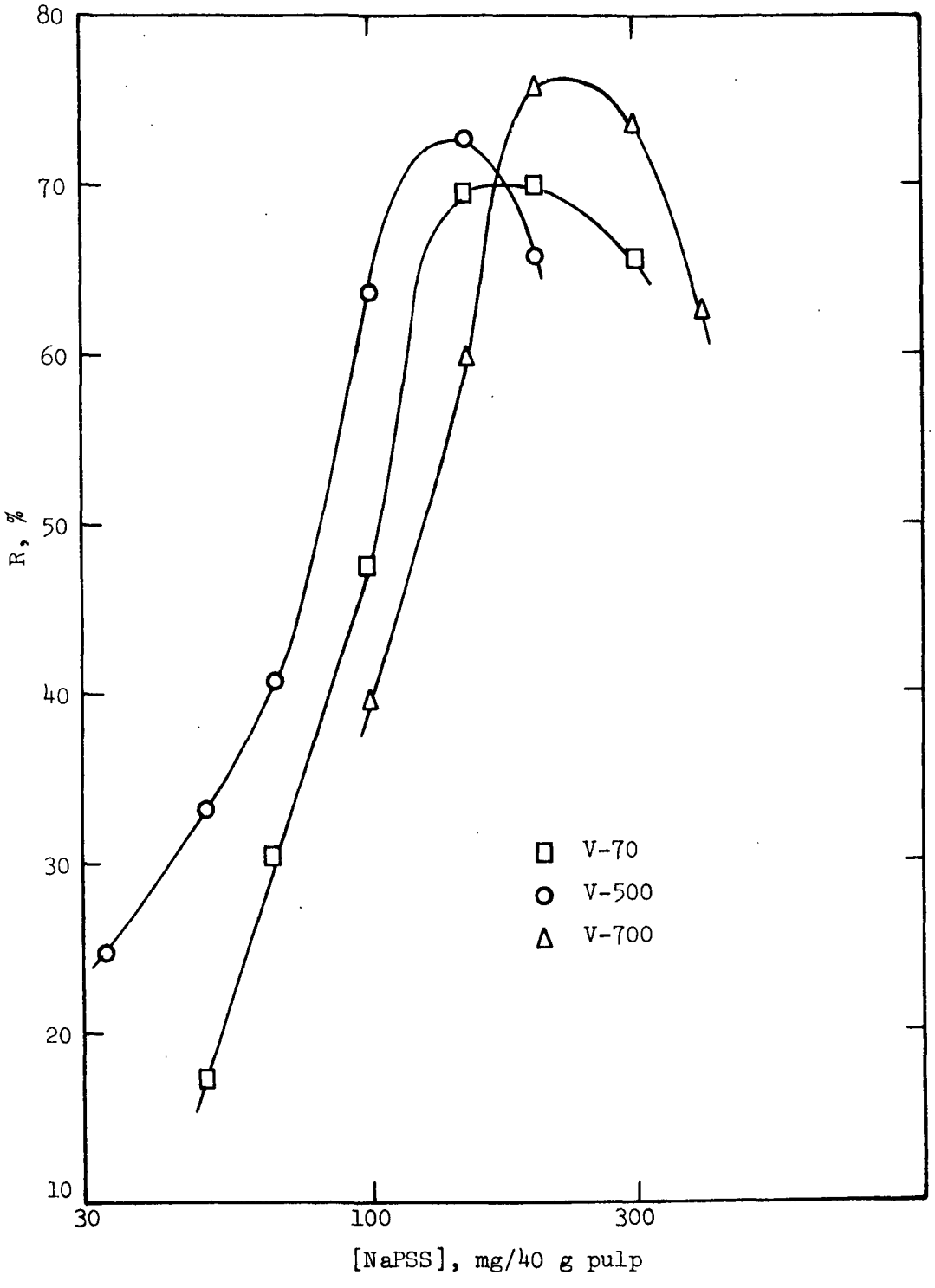

Figure 4. Semilogarithmic Plot of Percentage Retention Against Polymer Concentration for Three Samples of Sodium Polystyrene Sulfonate

weights of 0.07, 0.5, and 7 million, respectively. The three polymers appear to be about equally effective in producing a high level of retention. No clear trend of molecular weight vs. polymer concentration for optimum retention can be ascertained.

The specific scattering coefficients for these sheets, particularly at the high retention levels, fall considerably below those for Tydex 12 or other cationic retention aids at the same percentage retention. This suggests that, upon addition of the anionic polymer, considerable flocculation of the TiO_2 particles occurred before they became bound to the pulp surface. The result of the larger effective size of the TiO_2 particle is a reduced optical efficiency.

The Effect of Molecular Weight-Cationic Retention Aid
(Sets 110-112, 115-117, 119-121, 129-134)

The results of adding various amounts of the Dow series cationic polymers to the system are displayed in Fig. 5. For these experiments the polymer and the TiO_2 were mixed together without pH adjustment. (The pH was in the range 9-10 due to the basic character of the polyamine.) The TiO_2/polymer mixture was then added to the pulp, followed by adjustment of the pH to 5 with H_2SO_4, and subsequent sheet formation. All three polymers provide excellent retention. As found with the anionic polyelectrolytes in the previous section, there appears to be little effect of molecular weight on either the maximum retention possible or on the amount of polymer necessary to achieve that maximum. At the lowest polymer concentration the macromolecule with highest molecular weight is somewhat more efficient than the other two. However, as will be seen below, this particular sample (Set 119) yielded a rather low specific scattering coefficient indicating extensive preflocculation of the TiO_2. It must be concluded that the molecular weight of the polymer is not a strong factor in the retention process as judged by handsheet experiments.

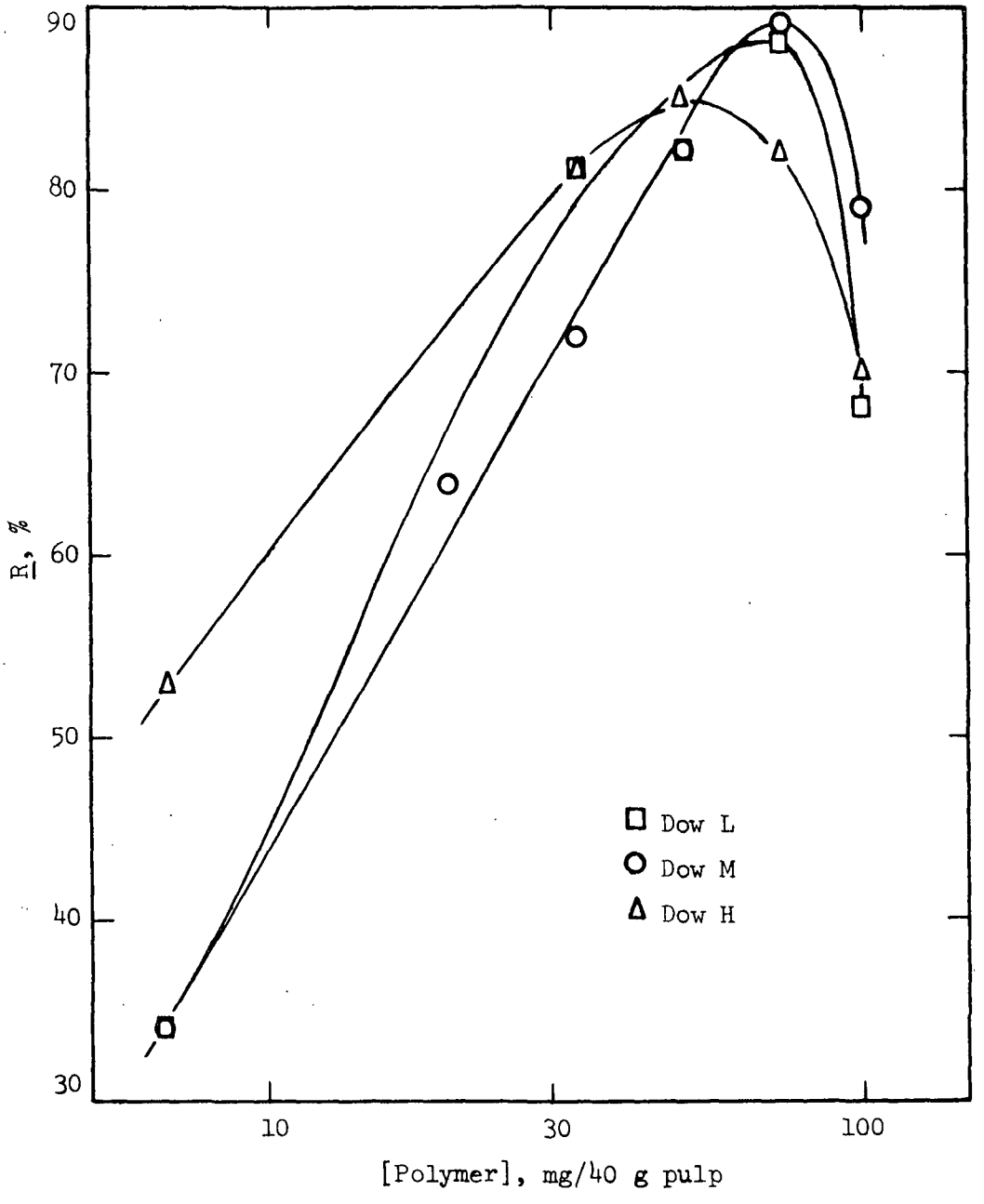

Figure 5. Semilogarithmic Plot of Percentage Retention Against Polymer Concentration for Three Cationic Polyacrylamides

Comparison of Various Cationic Retention Aids

The retention data for the various cationic polyelectrolytes are shown in Fig. 6. The results for Dow H and Dow L have been omitted for the sake of clarity and because they are represented reasonably well by those for Dow M. It is evident that considerable variation exists among the retention aids with respect to level of retention, breadth of concentration range over which the aid is effective, and polymer concentration at maximum retention. To evaluate the polymers from this (or similar) data for possible use in his mill, the papermaker must take a number of conflicting items into consideration. For example, (1) although chitosan is effective at lower dosage rates than the other polymers, can the overall system-pulp, water quality, other variables — be controlled well enough so that its narrow range of effectiveness is not a detriment? (2) Is it more economical to add sufficient polymer to achieve 60% (first pass) retention or to add more polymer to obtain the maximum retention possible? To answer this question other considerations such as white water reuse, saveall load, and a host of other factors that concern the overall papermaking system must be addressed. In addition, the properties of the sheets — opacity, brightness, strength, etc. — produced by the various possible addition levels of the several polymers would have to be evaluated to achieve maximum economic effect. The upshot of all this is that the information presented in Fig. 6 is only one of the many interconnected pieces needed for a final judgment.

The electrokinetic properties of the systems are presented in Fig. 7. Similar plots may be found in the literature (11) and have been called pulp titration curves. As noted previously (1) maximum retention is obtained at strongly negative values of the white water zeta potential so that data up to the isoelectric point ($\zeta = 0$) are available only for the furnish containing

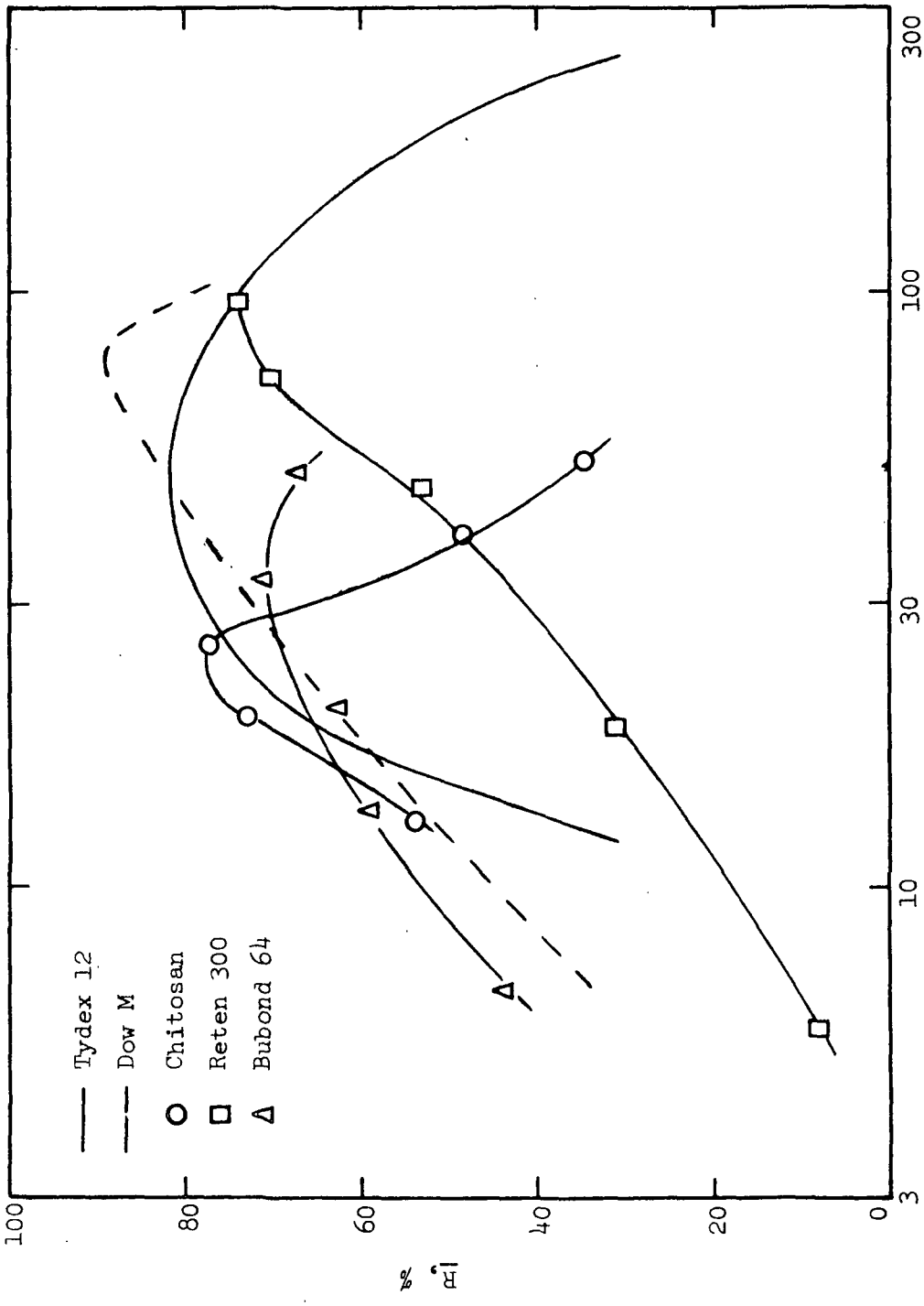

Figure 6. Semilogarithmic Plot of Percentage Retention Against Polymer Concentration for the Indicated Retention Aids

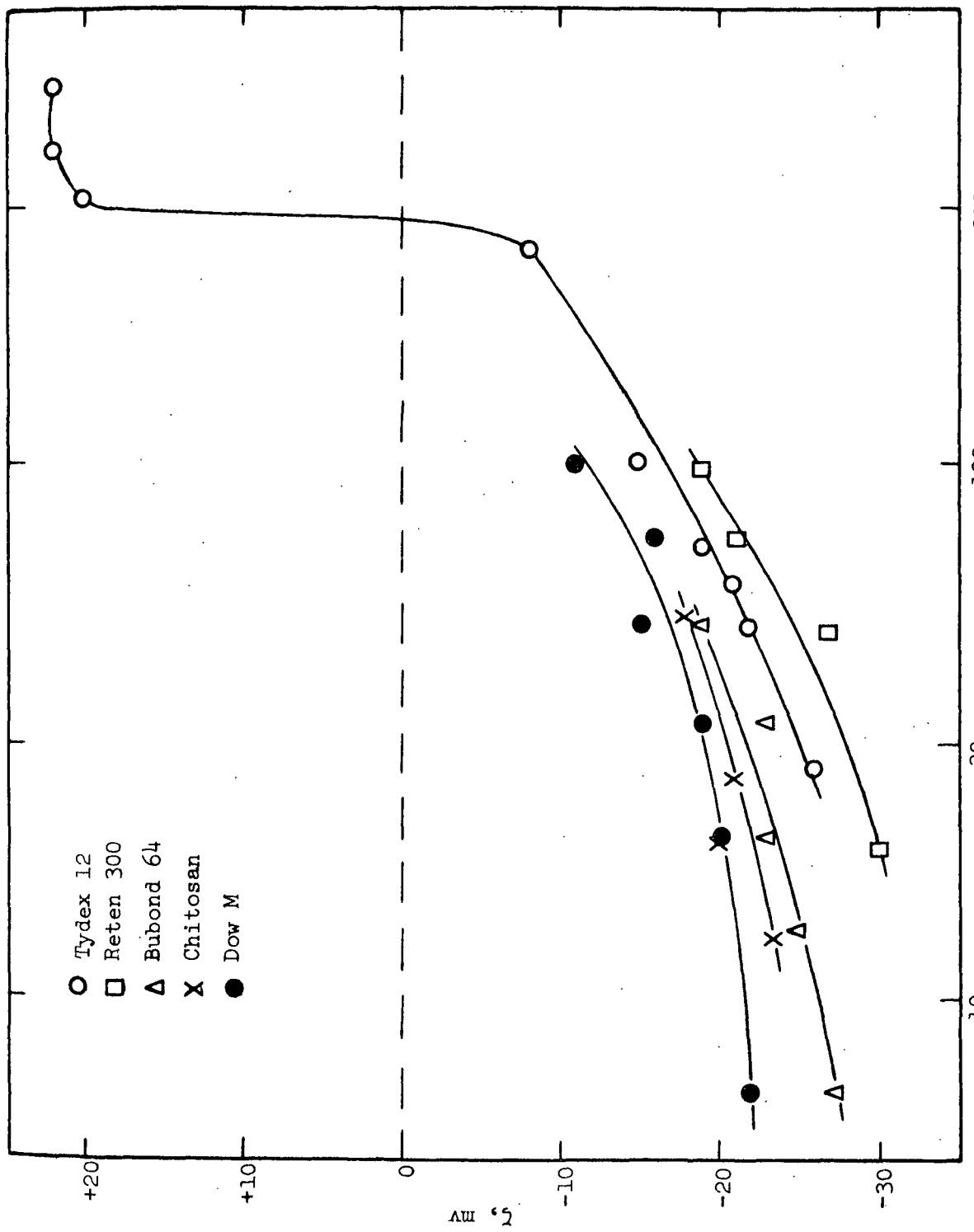

Figure 7. Semilogarithmic Plot of Zeta Potential Against Polymer Concentration for the Indicated Retention Aids

Tydex 12. The curves for the various polymers are all parallel, reflecting a similar mode of action upon the system. Earlier it was argued that because of the lack of a molecular weight effect the charge density of the polymer was the determining factor in the efficiency toward inducing flocculation. Similarly, the vertical displacements between the various systems are the product of different amounts of positive charge per unit mass and of different degrees of adsorption of the polymer onto the TiO_2 and pulp surfaces. This latter factor will be determined by the specific interaction forces between the polymers and the surfaces. Upon comparing the smooth, parallel trends of the electrokinetic properties of the several systems in Fig. 7 with the widely varying retention behavior of the same systems in Fig. 6, it is evident that zeta potential is not the only factor and probably not the most important factor in determining the extent of retention.

It is the opacity rather than the percentage retention that is the real concern of the papermaker. The relationship of these two parameters for the cationic retention aids is indicated in Fig. 8 where the specific scattering coefficient is plotted against retention. The different polymers have been given different symbols to determine whether there is a trend toward a positive or negative deviation from the average for a given material. The line was taken from Fig. 10 of the previous report (1) and represents a reasonably good linear fit of the data. As expected, the optical efficiency was dependent on the polymer system used. With few exceptions, sheets made with chitosan, Bubond 64, or Tydex 12 consistently showed scattering properties better than or equal to the arbitrarily drawn line. These do not represent the highest values of either R or s but only their ratio. The interpretation is that for these polymers the conditions in the system are such that flocculation of the TiO_2 particles before

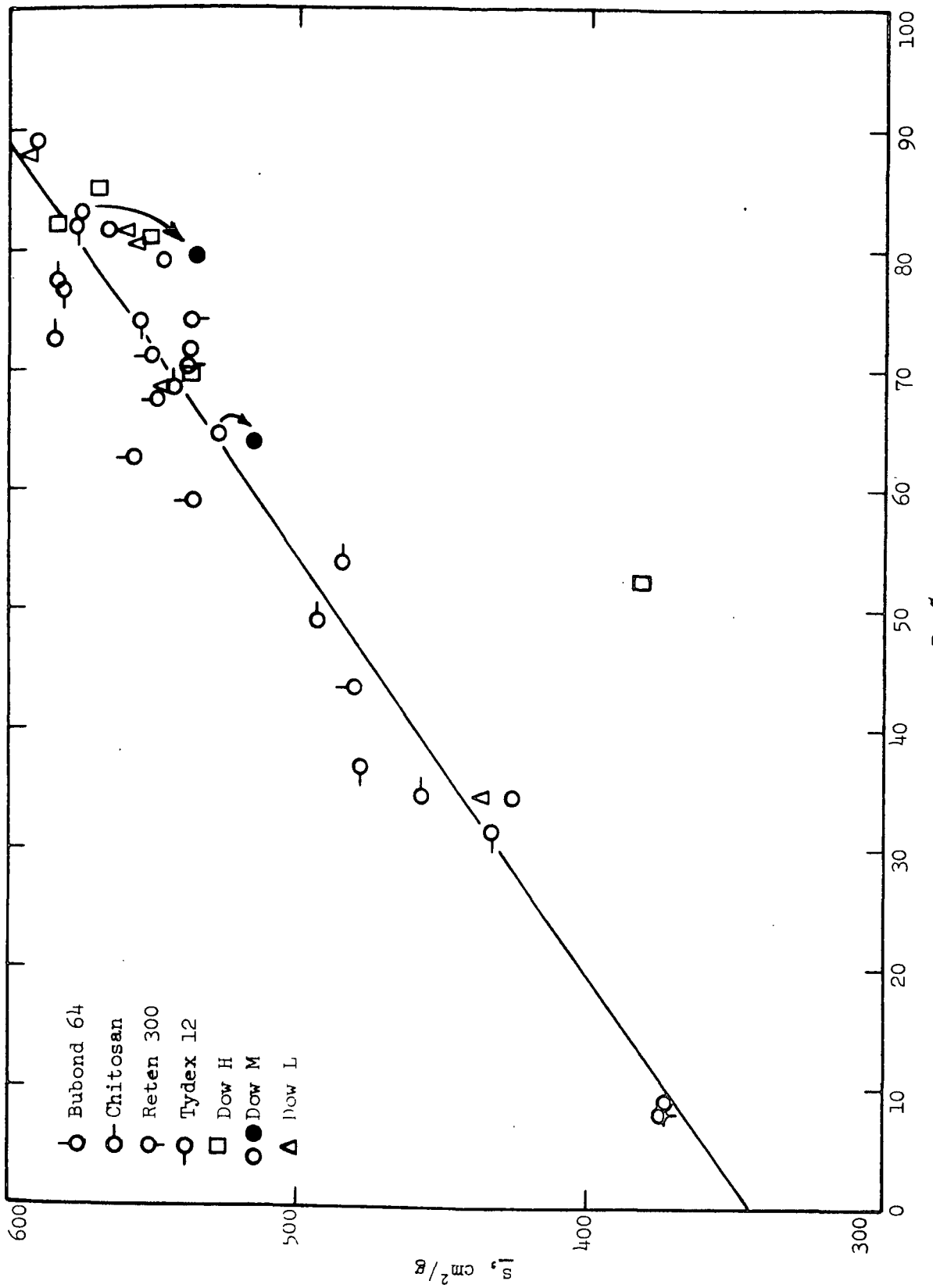

Figure 8. Specific Scattering Coefficient Plotted Against Percentage Retention for the Indicated Polymers. See Text for Details

deposition on the fiber surface is minimized and the filler remains in its most optically efficient form, i.e., individual particles of 0.15 μm diameter. The one exceptional low datum (Dow H) is that alluded to in the previous section. Here a small amount of retention aid was able to provide a reasonably good retention but at the expense of flocculation and dismal optical efficiency.

That the system conditions, and in particular the pH at the point of polymer addition, can have an important effect on the scattering can be seen in the results of Sets 138-141. Here Dow M was added at two different concentration levels and at two different points. For Sets 138 and 140 the polymer was added to the TiO_2 as described above, the pH was in the range 9-10, and the handsheets produced scattering which was close to the drawn average line and indicated by the tails of the arrows in Fig. 8. For Sets 139 and 141 the polymer was added to the mixture of pulp and TiO_2 and, because of the much greater dilution factor, the pH was considerably lower. These conditions resulted in some flocculation of the TiO_2 and, even though the retention remained approximately the same, the specific scattering coefficient decreased substantially as indicated by the arrows and black circles in Fig. 8. At the still lower pH of 5, massive flocculation occurs upon addition of the same amount of polymer to the TiO_2. These experiments are described in Part III.

A tentative explanation for this behavior can be offered. At the high pH in Sets 138 and 140 the polymer will be largely uncharged and at the high concentrations being used, will coat the particles acting as a protective colloid. Subsequently, when the filler is added to the pulp and the pH is adjusted to 5, the polymer will become highly positively charged and good retention onto the negatively-charged fibers will follow. In the case of Sets 139 and 141 the polymer is partially charged at the pH of mixing with the TiO_2,

and some flocculation occurs before enough polymer is adsorbed to provide restabilization. Upon adjustment of the pH to 5, further charging of the polymer takes place and good retention results. It is likely that the lower the pH the less polymer is adsorbed as was found for the PEI/TiO_2 system (1). This is borne out by the more negative zeta potentials found for Sets 139 and 141 compared with those for Sets 138 and 140. The conclusion to be drawn from these experiments is that it may be possible to improve the opacity of a sheet without attaining a higher retention by proper adjustment of the pH conditions at the point of polymer addition.

Effect of Concentration of TiO_2 (Sets 123, 124, 126, 128)

In the experiments described thus far the amount of TiO_2 in the furnish has been held constant at 5% based on the OD pulp. In order to reasonably extrapolate from these results to other conditions, it was necessary to study the effect of the TiO_2 concentration on the amount of polymer required for maximum retention. A series of sheets was made at a concentration of 10% TiO_2 in the furnish based on the OD pulp and with Tydex 12 as the retention aid. The results are listed in Table V along with the earlier results at the 5% level for comparison. The point of maximum retention for both TiO_2 concentrations is the same: near 50 mg Tydex/40 g pulp. The magnitudes of retention are similar at all polymer concentrations, and the zeta potentials are of the same magnitude. (The one zeta potential in parentheses does not follow the expected trend and is likely in error.) Hence, it may be concluded that at these TiO_2 addition levels, it is the concentration of fibers and fines and the electrokinetic charge on them that determines the percentage retention and the white water zeta potential and not the amount of TiO_2. This finding can also be surmised from the calculation of the amount of polyethylenimine that can adsorb

on the TiO_2 (based on the adsorption experiments in Progress Report Two) compared to the total amount of polymer in the furnish. Such a calculation shows that most of the polymer must end up on the fibers and fines. Thus, changing the amount of TiO_2 will have little effect and the results at the 5% TiO_2 level obtained elsewhere in this report can be generalized, with care, to other levels.

TABLE V

EFFECT OF TiO_2 CONCENTRATION ON RETENTION

[Tydex], mg/40 g pulp	TiO_2, % on OD pulp			
	5		10	
	R, %	ζ, mv	R, %	ζ, mv
27	77	-26	63	-23
50	82	-22	82	-15
100	74	-15	79	(-26)
200	47	-10	33	-10

Effect of Excess Salts (Sets 77, 78, 80-82)

Since most paper furnishes contain foreign ions from a variety of sources, it was deemed important to consider their influence in the present experiments. Handsheets were prepared with Tydex 12 at its optimum concentration (Fig. 6) and various amounts of either Na_2SO_4 or NaCl. The salts were added at every point of dilution so that their concentration remained constant throughout the stock preparation and sheetmaking process.

In many cases excess salts have been found to lower the zeta potential of a surface by collapsing the double layer and should thereby enhance retention. The data in Table VI show just the opposite effect.

TABLE VI

EFFECT OF SALTS
(50 mg Tydex 12/40 g pulp)

$[Na_2SO_4]$, M	R, %	ζ, mv
0	82	-22
0.001	73	-27
0.00167	67	-23
0.005	55	-21
[NaCl], M		
0.001	81	-19
0.005	73	-23

A monotonic decrease in retention results from increasing the salt concentration. It might be argued that the salt is collapsing the double layer and that the steady decrease in R is a product of the increasing overdosage with the polymer. However, the values of the zeta potential do not bear out this interpretation. Rather, they suggest ion binding as the explanation. It is well known that polyethylenimine binds chloride ion (7, 12), and there is indirect evidence for sulfate ion binding (13). A protonated amine group together with its bound chloride ion would present a net zero charge at some distance from the site. Likewise a protonated amine group with a bound sulfate ion would yield a net negative charge. For the case of addition of 0.001M Na_2SO_4, retention is depressed due to the decreased effective positive charge on the Tydex 12 resulting from sulfate ion binding. The zeta potential concomitantly attains a larger negative value. Larger additions of Na_2SO_4 reduce the retention still more while the zeta potential exhibits a trend toward smaller negative values, the result of double layer compression by the excess ions in solution.

A similar trend in the retention is seen for the case of addition of NaCl although the interpretation of the zeta potentials is not clear. Evidently, excess amounts of sulfate and chloride ions (and probably other anions) are detrimental to the retention process.

In another set of experiments to confirm the existence of ion binding for this system, PEI was adsorbed on TiO_2 at a pH of 9 under conditions yielding a high surface coverage. The sample was then divided into two parts and the pH of each was adjusted to 5 with HCl in the one case and H_2SO_4 in the other. At this lower pH the PEI is strongly protonated and the zeta potentials of the TiO_2/PEI systems were +44 for the HCl case and +26 for the other. The bound sulfate ion causes a considerable reduction in the zeta potential.

On the Origin of the Large Negative Zeta Potential

As noted in the previous report (1) and evident in Table IV here, the white water zeta potentials for the systems with best retention are large and negative, typically -16 to -22 mv. In view of the flocculation experiments in Part I where only minor amounts of cationic polymers were necessary for efficient flocculation and the particle's zeta potential under these conditions was little affected by the polymer's presence, the present results are not unusual. As will be further discussed, the disturbing feature in the handsheet studies is that the TiO_2 particles are initially made strongly positive with adsorbed, protonated cationic polymers but exhibit strongly negative zeta potentials in the white water.

Several possible explanations for this behavior will be considered. In light of the findings in the previous section on counterion binding, it might be thought that the negative zeta potential could arise from adsorption of sulfate

ions (from the H_2SO_4 for pH adjustment) during the stock preparation. However, an experiment (Set 108) using HCl for pH adjustment gave a similar zeta potential (-24 mv) and even produced decreased retention (cf. Set 42). The sulfate ion is not the culprit.

It should be emphasized at this point that the electrophoretic mobility measurements are made on (apparently) individual TiO_2 particles in the white water. Fines with retained TiO_2 can also be observed and usually travel with the same velocity as the individual TiO_2 particles.

Another possibility concerns the very small fines or even "soluble fines." By these we mean fiber fragments too small to be observed with the (light) microscope. Since these would be expected to carry a negative charge, they could adsorb onto the TiO_2 particles coated with positively charged polyethylenimine (or other cationic polymer), thereby reversing the charge. This could happen wherever the TiO_2 particles were: retained on fiber, retained on fines, or "free" and would explain the ubiquitous value of approximately -20 mv for the zeta potential.

Several experiments to test this hypothesis were performed. The method chosen was to try to reduce or eliminate the submicroscopic fines. A sample of the pulp was classified in an attempt to wash out the fines and an experiment was performed with regenerated cellulose fiber which should have no fines. Handsheets were formed from these pulps and the zeta potential of the TiO_2 particles was measured on samples taken at various points in the stock preparation. These were: 1. The furnish at 1 1/2% consistency after addition of all components and adjustment of the pH to 5 with H_2SO_4, 2. The furnish after dilution to 1/2% consistency, and 3. The furnish after dilution to 0.04% consistency in the

decklebox or equivalently the white water from sheet formation. One run was also made with all components present except the pulp. The results are listed in Table VII.

TABLE VII

ZETA POTENTIAL THROUGHOUT STOCK PREPARATION
(5% TiO_2 on pulp, 50 mg PEI/40 g pulp)

Pulp	Zeta Potential, mv Consistency		
	1 1/2%	1/2%	0.04%
Standard	+17	∿0	-17
Classified	+21	-22	-22
Rayon	+17	+18	-27
None	+26	+26	+16

The TiO_2 in all the systems is moderately positive at the 1 1/2% consistency level. The trend with dilution is toward decreasingly positive and, in the cases with pulp present, eventually negative zeta potentials. It can be argued that, even for a classified pulp, it is not possible to remove all the fines, and that any subsequent agitation of the pulp will produce new fines (14). This should not be the case for the rayon fibers, yet here, too, there is a change in the zeta potential from positive to negative during the final dilution. Even the system with no pulp present exhibits a decrease at this point although remaining on the positive side. It is apparent that the hypothesis of adsorption of submicroscopic fines onto the PEI-coated TiO_2 particles, while able to explain some of the electrokinetic and retention phenomena, is inadequate. Another mechanism, unavailable at present, must be invoked to explain the data of Table VII.

CONCLUSIONS

Based on studies of both cationic and anionic retention aids, it was found that polymer molecular weight had little effect on the efficiency of retention as judged by handsheet formation. Particlar care must be taken to adjust the system conditions before polymer addition so that flocculation of the TiO_2 will not occur before adsorption on the fiber and optical efficiency will be at a maximum. At normal addition levels of TiO_2 the amount of polymer required for good retention is more a function of the pulp than of the amount of TiO_2. Polyvalent anions are likely to be detrimental to retention when cationic polyelectrolytes are used because of counterion binding. The origin of the large negative zeta potential found under conditions of maximum retention remains an enigma.

PART III. RETENTION STUDIES USING THE PRESSURE SHEET MOLD

MATERIALS AND METHODS

The experiments in this part were carried out on a modification of the dynamic drainage tester (15). Because the configuration of the apparatus has been changed a good deal and the present use is somewhat different from that of the original, it seems appropriate to describe it in terms of its function. Hence, it will be designated as the pressure sheet mold.

Early experiments showed that it was not possible to recover wrinkle-free sheets for optical measurements from the apparatus in the original configuration, that is, with the piston traveling upward to form a sheet on the underside of the wire placed at the top of the tube. The instrument was therefore redesigned, essentially turning the sheet-forming section upside down (or right side up, depending upon how you look at it). As with the original, it consists of a 3-inch nominal inside diameter Lucite forming tube about 1 m in length on the lower end of which is mounted (present configuration) the 3-inch diameter 100-mesh bronze wire. A schematic is shown in Fig. 9. The tube is filled from the bottom, the cover under the wire is removed, and the travel of the constant velocity piston is started. The piston stops about 1 inch above the wire and the remainder of the water is drawn through the formed sheet by aspiration. The wire is then demounted from the tube, and the sheet is couched onto a blotter by using a brass roll. The sheets were pressed between blotters for 5 minutes at 50 psi and dried on a steam drum for 7 minutes at 220°F.

The (constant) velocity of the piston can be varied from less than 5 to about 100 cm/sec. For the present pulp it was not possible to exceed about 25 cm/sec because of leakage around the wire mount at the higher pressures. For the

experiments below, three speeds were chosen: nominally 5, 12, and 23 cm/sec. The highest of these corresponds to the drainage rate calculated for a typical paper machine operating at about 2000 ft/min (16). The lowest speed is approximately that of the average drainage rate of this pulp during handsheet formation on the Noble & Wood sheet mold with 100-mesh wire (Part II above).

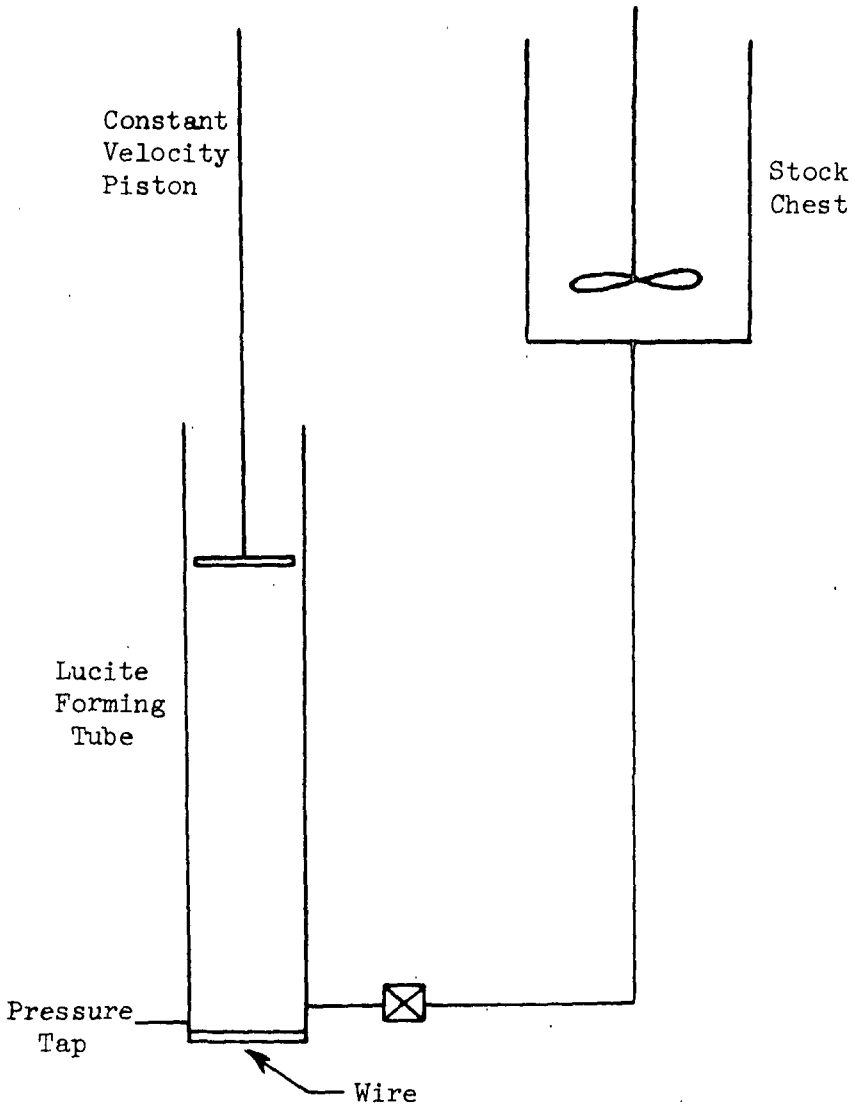

Figure 9. Schematic of the Pressure Sheet Mold

To prevent fiber flocculation in the tube during sheet formation and to prevent excessive pressure drop across the wire it is necessary to work with extremely dilute suspensions, in the present case 0.005% consistency. This concentration produces a sheet with a basis weight of 50 g/m^2.

A pressure tap about 1/4 inch above the wire allows the pressure drop across the wire to be measured thereby giving an indication of the drainage properties of the furnish. The tap was connected to a Pace pressure transducer whose signal was fed to an Esterline Angus recorder. In this way the exponential build-up of pressure during sheet formation could be monitored. For comparative purposes only the peak pressure will be discussed below. Because it was not possible to set the piston velocity exactly the same each time, the pressure-time recording was also useful in determining the actual speed.

In general, the stock was prepared at the concentrations used for the handsheet work described earlier, i.e., 1 1/2% consistency. This was subsequently diluted to 100 liters (0.005% consistency) in a stirred, teflon-lined tank. This quantity of stock was sufficient for the formation of 18 sheets, 6 at each of 3 speeds.

Tydex 12, the combination Tydex 12 with the V series NaPSS polymers, and the Dow series of cationic polyacrylamides were studied as the retention aids at several addition levels using the earlier handsheet work as a guide. As with the handsheet experiments, the Tydex 12 was added to the TiO_2 which was then added to the pulp. The NaPSS, if used, was subsequently added to the pulp and mixed in for 5 minutes before dilution to 100 liters.

For the Dow series it was deemed useful for later analysis to carry out the mixing of the polymer and TiO_2 under the same conditions as those for

the adsorption experiments discussed in Part I, viz. a pH of 5. However, massive flocculation resulted. The procedure was modified so that the pulp and TiO_2 were mixed together at a pH of 5, and the polymer was then added. Even under conditions of vigorous stirring, some flocculation of the TiO_2 occurred before it was retained on the fibers, as seen by reduced optical efficiency and visual observation by scanning electron microscope.

RESULTS AND DISCUSSION

The retention and scattering data for the sheets with various additives are listed in Table VIII. In general, the retentions achieved with sheets formed on the pressure sheet mold are quite comparable to those obtained earlier in the handsheet work at the same level of addition of retention aid. The specific scattering coefficients for the present sheets are somewhat lower than the handsheet values for two reasons. 1) The scattering of the unfilled sheet (314 cm^2/g) is about 30 cm^2/g less than the value for the handsheet. There is no ready explanation for this behavior, but the effect is mirrored in the data for Tydex 12 which are also about 30 cm^2/g lower than the corresponding handsheet values at the same degree of retention. 2) Because of the partial preflocculation of the TiO_2 by the Dow series as noted above, the specific scattering coefficients for sheets containing these polymers are lower still than those for the sheets containing Tydex 12. Sheets containing Tydex 12 plus V-70 correlate well with those containing only Tydex 12; however, those with the combination Tydex 12 plus V-700 are low suggesting some preflocculation of TiO_2 by this very high molecular weight polymer.

TABLE VIII

PROPERTIES OF SHEETS FROM PRESSURE SHEET MOLD

Additive		Nominal Piston Velocity,		
Type	Amount, mg/40 g pulp	cm/sec	R, %	S, cm^2/g
None	— No TiO_2 —	5	--	312
		12	--	317
		23	--	312
Tydex 12	50	5	74	530
		12	71	502
		23	68	501
Dow H	12	5	52	439
		12	52	421
		23	45	411
Dow H	24	5	64	474
		12	65	449
		23	58	446
Dow H	48	5	75	493
		12	71	478
		23	63	471
Dow M	12	5	51	452
		12	48	444
		23	43	440
Dow M	24	5	69	490
		12	64	462
		23	57	457
Dow M	48	5	64	482
		12	61	477
		23	55	457
Dow L	12	5	56	436
		12	52	420
		23	48	415
Dow L	24	5	60	463
		12	55	450
		23	51	435
Dow L	48	5	55	468
		12	52	451
		23	49	438

TABLE VIII (Continued)

PROPERTIES OF SHEETS FROM PRESSURE SHEET MOLD

Additive		Nominal Piston Velocity,		
Type	Amount, mg/40 g pulp	cm/sec	R, %	s, cm^2/g
Tydex 12	320	5	50	451
V-70	144	12	48	453
		23	48	448
Tydex 12	320	5	55	473
V-70	192	12	53	459
		23	49	443
Tydex 12	320	5	70	477
V-70	288	12	65	472
		23	62	472
Tydex 12	320	5	46	416
V-700	144	12	46	418
		23	40	409
Tydex 12	320	5	72	482
V-700	192	12	70	472
		23	69	464
Tydex 12	320	5	81	480
V-700	288	12	81	470
		23	75	463

There is a trend in all of the furnishes for the retention to decrease with increasing drainage rate. Whether this represents a washing off of particles already retained in the sheet being formed by the hydrodynamic shearing forces or whether unretained particles in the stock are forced past the fibers in the sheet so quickly as to prevent coflocculation, it is not possible to say. Probably both explanations have some validity. The magnitude of the decrease depends on the polymer system used and also on the polymer dosage level (or perhaps the retention level).

The results for the Dow series are shown in Fig. 10. The sensitivity to shearing as measured by the vertical displacement of the curves at different drainage rates does not appear to be a function of molecular weight. The overall level of retention does depend on molecular weight. The medium and high molecular weight polymers produce considerably higher retention than does the low molecular weight material, at least over the concentration range covered here.

Similar features can be seen for the Tydex 12 plus V-series NaPSS in Fig. 11. Here the vertical bars represent the range of values obtained at a given polymer addition level and the three piston velocities. Again for the range of polymer concentrations encompassed, there appears to be little dependence of shear sensitivity, but an appreciable effect on retention level, caused by the 100-fold difference in molecular weights. Here, also, the higher molecular weight material produces the higher retention. It must be cautioned, however, that the concentration range covered is rather limited and generalizations regarding the effect of molecular weight are probably not warranted.

During sheet formation data were also generated on the drainage properties of the furnishes. As a measure of these, the ratio of maximum pressure drop to piston velocity may be compared for the different systems at some particular piston velocity. There was about a 30% decrease in resistance to drainage upon going from the pulp alone to a furnish containing any of the retention aids. No trends could be discerned concerning the relative efficacies of the various additives nor on the effect of dosage level of the additives. Variations were noted but appeared to be within the experimental error of the method. It is likely that lower addition levels of the polymers than those used here would reveal the incremental decreases from the pulp-alone values.

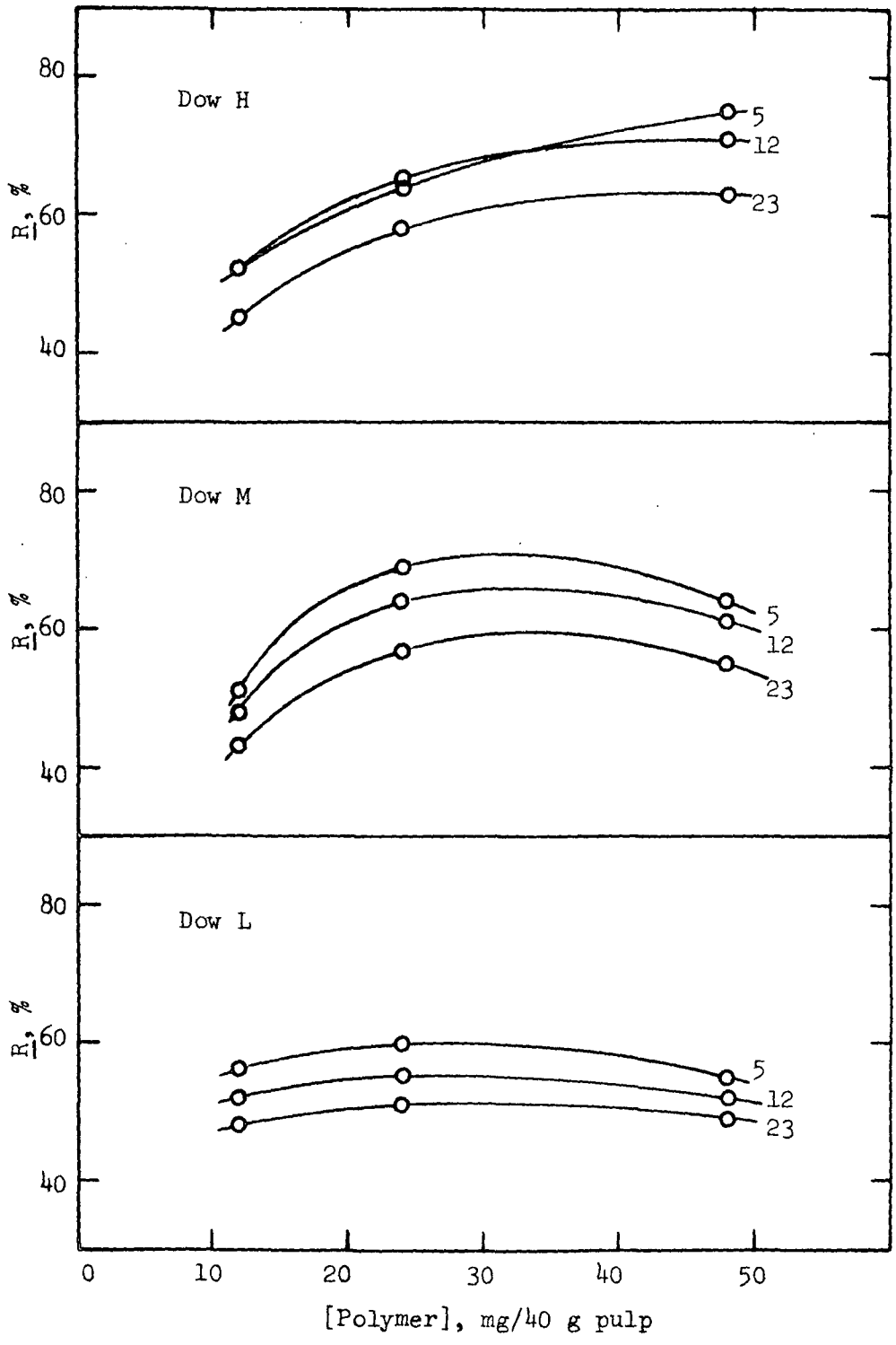

Figure 10. Percentage Retention Plotted Against Concentration of the Cationic Polyacrylamides at the Indicated Nominal Piston Velocities

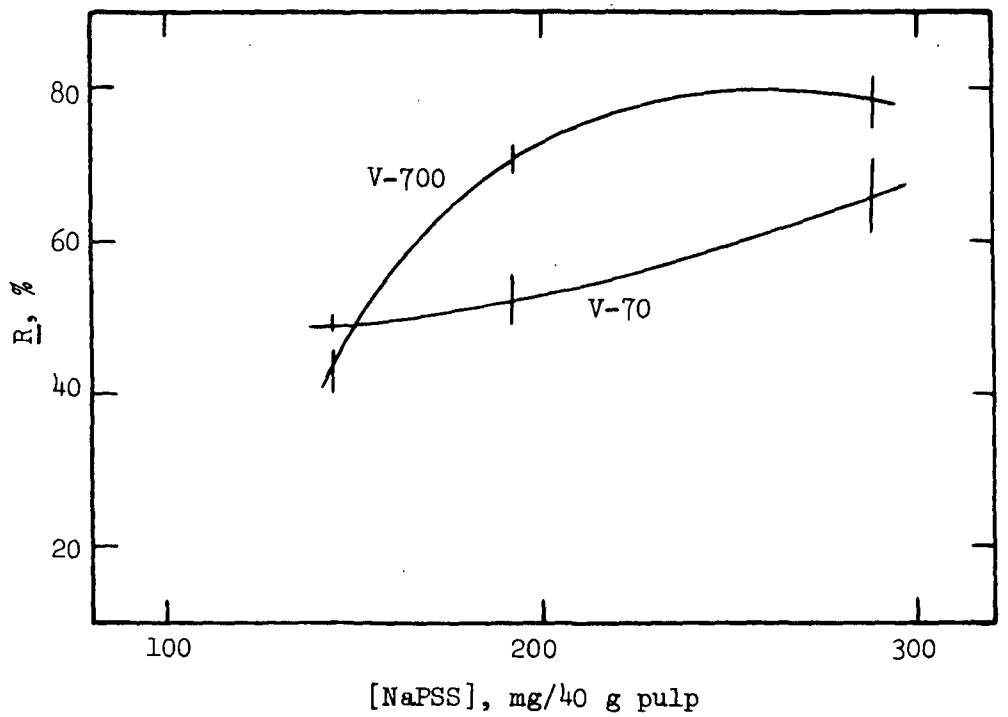

Figure 11. Percentage Retention Plotted Against Concentration of the Indicated Sodium Polystyrene Sulfonates. TiO_2 was Pretreated with 320 mg Tydex 12/40 g Pulp. Vertical Bars Show Range of Valves for the Various Drainage Rates

ACKNOWLEDGMENTS

The author is pleased to acknowledge the assistance of N. L. Colson, who carried out the measurements of adsorption, flocculation, and zeta potential and prepared sheets on the pressure sheet mold. Mr. Colson collaborated on the redesign of the dynamic drainage tester with O. Kuehl, who also fabricated the parts necessary for the modification. The advice of B. D. Andrews on operating the apparatus and his help in calibrating the pressure transducer and the piston velocities are gratefully acknowledged. Thanks are also due to D. Gilbert, who prepared the handsheets, and to many others at The Institute of Paper Chemistry, who analyzed the sheets for optical, retention, and strength properties.

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